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(54) PIEZOELECTRIC PORCELAIN COMPOSITION FOR CERAMIC FILTER DEVICE EXCELLENT IN MOISTURE RESISTANCE

(57)Abstract:
PURPOSE: To obtain a piezoelectric porcelain compsn. using a compsn. different from that of PZT as a base, having high Kr and having low Qm even at high humidity.
CONSTITUTION: A basic compsn. represented by the general formula, xPb(Mg3/1 Nb2/3)O3-yPbTiO3 (where 0.05≤x≤0.50, 0.25≤y≤ 0.50 and 0≤z≤0.625) is prepd. and NiO is incorporated into the basic compsn. by >0 to 5wt.%.

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(54)【発明の名称】　耐湿性に優れたセラミックフィルタ素子用圧電磁器組成物

(57)【要約】
【目的】ＰＺＴとは異なる組成を基本とし、Ｋｒが高く且つ高湿度下でもＱｍが小さいセラミックフィルタ素子用圧電磁器組成物を提供する。
【構成】一般式がｘＰｂ（$Mg_{1/3}Nb_{2/3}$）O_3－ｙＰｂＴｉO_3－ｚＰｂＺｒO_3で示され、０．０５≦ｘ≦０．５０、０．２５≦ｙ≦０．５０、０≦ｚ≦０．６２５からなる基本組成物に対して、ＮｉＯを５重量%以下（ただし０を除く）含有することを特徴とする。

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【特許請求の範囲】

【請求項１】　一般式がｘＰｂ（$Mg_{1/3}Nb_{2/3}$）O_3－ｙＰｂＴｉO_3－ｚＰｂＺｒO_3で示され、０．０５≦ｘ≦０．５０、０．２５≦ｙ≦０．５０、０≦ｚ≦０．６２５からなる基本組成物に対して、ＮｉＯを５重量％以下（ただし０を除く）含有することを特徴とする耐湿性に優れたセラミックフィルタ素子用圧電磁器組成物。ただし、一般式中、ｘ、ｙ及びｚは、ｘ＋ｙ＋ｚ＝１を充足する数である。

【請求項２】　フィルタがラダーフィルタである請求項１に記載の耐湿性に優れたセラミックフィルタ素子用圧電磁器組成物。

【請求項３】　ｘ＝０．３７５、ｙ＝０．３７５、ｚ＝０．２５０からなる第一の組成と、ｘ＝０．２５０、ｙ＝０．３７５、ｚ＝０．３７５からなる第二の組成とで挟まれる相転移境界線上であって、第一の組成に近い組成物を並列共振子、第二の組成に近い他の組成物を直列共振子とする請求項２に記載の耐湿性に優れたセラミックフィルタ素子用圧電磁器組成物。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】この発明は、耐湿性に優れたセラミックフィルタ素子用圧電磁器組成物に関する。この圧電磁器組成物は、セルラー用超薄型フィルタ、ページャ用薄型フィルタなどのように、中間周波数が４５５ｋＨｚであるラダーフィルタに好適に利用され得る。

【０００２】

【従来の技術】この種の圧電磁器組成物としては、位相歪が小さく、かつ誘電率εｒと径方向電気機械結合係数Ｋｒができるだけ高く、更に耐湿負荷試験に対する機械的品質係数Ｑｍ及びその変化率ができるだけ小さいものが望まれている。これらの要望のいくつかを達成する目的で相転移境界線（ＭＰＢ）近傍の組成を有するチタン酸ジルコン酸鉛Ｐｂ（Ti_xZr_{1-x}）O_3（以下、ＰＺＴと略記する。ただし、ｘ＝０．４～０．６である。）を基本組成とし、種々の添加物によって各々の特性を微調整しようとする提案がなされている。

【０００３】例えば、特開平５－９０７２号公報には、酸化クロムと酸化鉛の反応生成物の内、Pb_2CrO_5よりもPb_3CrO_8の多いＰＺＴ組成物とすることにより耐湿性を向上させたセラミックフィルタ素子用圧電磁器組成物が記載されている。また、特開平５－１４８０１６号公報には、ＰＺＴのＰｂ原子の一部をＢａ等で置換してＭＰＢよりも正方晶系強誘電体相側の領域を基本組成とし、これにＳｂ等のソフト化剤及びＣｏ等のハード化剤を微量添加することにより、Ｋｒを大きく且つ高温でのＫｒの劣化率を小さくしたセラミックフィルタ素子用圧電磁器組成物が記載されている。

【０００４】

【発明が解決しようとする課題】しかし、特開平５－９０７２号公報に記載のものは、Ｋｒについての検討がなされていない。また、特開平５－１４８０１６号公報に記載のものは、耐湿性の検討がなされていない。更にいずれもＰＺＴを基本組成としているので、圧電特性に関してＰＺＴを越えるものではない。

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【０００５】この発明の目的は、ＰＺＴとは異なる組成を基本とし、Ｋｒが高く且つ高湿度下でもＱｍが小さいセラミックフィルタ素子用圧電磁器組成物を提供することにある。

【０００６】

【課題を解決するための手段】その目的を達成するために、この発明のセラミックフィルタ素子用圧電磁器組成物は、一般式がｘＰｂ（$Mg_{1/3}Nb_{2/3}$）O_3－ｙＰｂＴｉO_3－ｚＰｂＺｒO_3で示され、０．０５≦ｘ≦０．５０、０．２５≦ｙ≦０．５０、０≦ｚ≦０．６２５からなる基本組成物に対して、ＮｉＯを５重量％以下（ただし０を除く）含有することを特徴とする。ただし、一般式中、ｘ、ｙ及びｚは、ｘ＋ｙ＋ｚ＝１を充足する数である。

【０００７】

【作用】上記基本組成物は、Ｑｍが低く、Ｋｒが高い。しかもＭＰＢ上でεｒが変化するので、例えばラダーフィルタにおいて並列用、直列用等その用途に応じて基本組成を変えることにより適当なεｒを選択することができる。そして、この基本組成物にＮｉＯを所定量添加すると、Ｑｍを下げながらεｒとＫｒを向上させ、更にＱｍの耐湿特性も向上させることができる。尚、本発明の一般式中、ｘ，ｙ，ｚをそれぞれ上記の特定範囲に限定した理由は次の通りである。

【０００８】即ち、ｘが０．０５に満たないと焼結性が悪く、０．５０を越えると高いＴｃが得られない。また、ｙが０．２５に満たないと高いＴｃが得られず、０．５０を越えると高いεｒ，Ｋｒが得られない。更にｚはゼロでも実用上問題ないが、０．６２５を越えると高いＴｃが得られない。更にこれら基本組成に添加するＮｉＯは、その添加量が増えるに従いＴｃが低下するので最大５重量％までとした。

【０００９】

【実施例】

－実施例１－

本例は、基本組成の範囲を確定するとともに、この発明の圧電磁器組成物の製造方法とＮｉＯの添加効果を例示するものである。

【００１０】［基本組成の確定及び製造方法］純度９９．３％の酸化鉛ＰｂＯ、純度９９．４％の酸化マグネシウムＭｇＯ、純度９９．５％の酸化ニオブNb_2O_5、純度９８．５％の酸化チタンＴｉO_2及び純度９９．０％の酸化ジルコニウムＺｒO_2を表１及び図１に示す組成Ｎｏ．１～１３の組成に対応する調合割合でそれぞれ調合し、アルミナ玉石とともに振動ミルにて乾式混合粉

砕し、混合物を８５０℃で２時間仮焼した後、ポット回転機にてアルミナ玉石のほかイオン交換水、有機質結合剤等とともに９０ｒｐｍで２３時間湿式混合することによってスラリーを得た。なお、図１中、Ｔは強誘電正方晶（ferroelectric tetragonal）、Ｒは強誘電菱面体晶（ferroelectric rhombohedral）、ＰＣは強誘電擬立方晶（ferroelectric pseudocubic）の省略記号である。

【００１１】スラリーを０．４Ｔｏｒｒ以下の真空中、－４０℃で凍結乾燥し、孔径５００μｍの篩いを通過させた後、１ｔ／ｃｍ²の圧力で直径２５ｍｍ×厚さ２ｍｍの円板状に成形し、１３００℃で２時間焼成した。続いて焼成体を厚さ１ｍｍになるまで研磨した後、Ａｇペ＊

＊ーストにてその両主面に直径１８ｍｍの電極パターンをスクリーン印刷し、７２０℃で焼き付けた。そして、これを１００℃～１５０℃のシリコンオイル中に浸漬し、電極間に３０ｋＶ／ｃｍの直流電圧を３０分印加することによって分極し、セラミックフィルタ素子用圧電磁器とした。以上の製造工程は、後述の各々の例においても、調合段階で添加物が追加されることを除いて同様である。得られた圧電磁器についてεr、Qm、Kr及びTcを測定した結果を表１に示す。

【００１２】

【表１】

組成 No.	組成［mol分率］ PMN	PT	PZ	Qm	Kr［%］	εr	Tc［℃］
1	.500	.500	0	３２０	２２	８９０	２５３
2	.375	.500	.125	３３０	１５	７００	２８３
3	.250	.500	.250	３３０	１６	８００	３１６
4	.125	.500	.375	３２０	１７	９００	３５１
5	.500	.375	.125	１００	４６	３２００	２１３
6	.375	.375	.250	１７０	５６	２０００	２４５
7	.250	.375	.375	１５０	３０	７７０	２７８
8	.125	.375	.500	１８０	２４	７００	３１３
9	.500	.250	.250	１９０	４２	８４０	２２６
１０	.375	.250	.375	２００	４０	６４０	２０６
１１	.250	.250	.500	２２０	３４	５００	２６３
１２	.125	.250	.625	２５０	１９	５３０	２９３
１３	.050	.450	.500	１７０	４８	１２００	３６６

［注］表中、PMN、PT及びPZは、それぞれ$Pb(Mg_{1/3}Nb_{2/3})O_3$、$PbTiO_3$及び$PbZrO_3$を表す。

表１にみられるように本発明の基本組成範囲、特にそのＭＰＢ付近の組成Ｎｏ．５，６において、Qmが小さく、Krが高く、εrも高い。また、組成Ｎｏ．６と組成Ｎｏ．７との間でεrが急変していることも判った。従って、この２点を結ぶ線上の組成のうち、Ｎｏ．６に近い側を並列共振子用、Ｎｏ．７に近い側を直列共振子用として選択すれば、Qmをできるだけ小さく、Krをできるだけ高く維持しながら、所望のεrを具備する磁器が得られることが明らかである。

【００１３】［ＮｉＯの添加例］上記の組成Ｎｏ．６となるように秤量した原料１００％に対して、純度９７％のＮｉＯを所定量添加した以外は、上記と同様の方法にてセラミックフィルタ素子用圧電磁器を製造した。このセラミックフィルタ素子用圧電磁器について、εr、Kr、Qm及びキュリー点Tcを測定した結果を表２に示す。

【００１４】また、６０℃、相対湿度９５％の雰囲気中でのQmの初期値に対する経時変化率（％）を測定した結果を表３、図２及び図３に示す。図中、「６無添加」とは、組成Ｎｏ．６に何も添加していないことを現し、「６＋ＮｉＯ」とは、組成Ｎｏ．６にＮｉＯを添加したことを現す。尚、図２のデータを表記しなかったが、初期値に対して２０％減少したところで定常状態となっていることが図２から明らかである。

【００１５】

【表２】

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＊【表３】

NiO量 [wt%]	εr	Kr[%]	Qm	Tc[℃]
0．2	２３００	５７	１２０	２４２
0．5	２６００	５９	１００	２３７
1．0	２９００	６１	９５	２３０
3．0	３１００	５６	１００	２２１
5．0	３２００	５５	１００	２０５

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時間 [hr]	素子	ＮｉＯ添加量［重量%］ 0．2	0．5	1．0	3．0	5．0
初期	A	125	107	95	101	102
	B	117	107	97	95	99
114	A	-5	-4	-5	-9	-3
	B	-5	0	-5	-5	-5
280	A	-7	-4	+2	-3	-3
	B	-3	-4	+2	+5	-3
446	A	-10	+6	-2	-4	+2
	B	-7	-5	-7	+1	-4
1043	A	-4	+6	+3	+3	0
	B	-3	+5	+2	+8	+1

表２、表３、図２及び図３にみられるように、基本組成Ｎｏ．６にＮｉＯを所定量添加しただけで、Ｑｍを下げながらεｒとＫｒを向上させ、更に高湿度下でのＱｍの経時変化を抑制することができた。

【００１６】－実施例２－

本例は、実施例１の基本組成Ｎｏ．７にＮｉＯを添加したセラミックフィルタ素子用圧電磁器について、その諸特性を評価したものである。すなわち、前記表１及び図１の組成Ｎｏ．７となるように秤量した原料１００％に対して、純度９７％のＮｉＯを所定量添加した以外は、実施例１と同様の方法にてセラミックフィルタ素子用圧電磁器を製造した。このセラミックフィルタ素子用圧電磁器について、εｒ、Ｋｒ、Ｑｍ及びキュリー点Ｔｃを測定した結果を表４に示す。

【００１７】また、６０℃、相対湿度９５％の雰囲気中でのＱｍの初期値に対する経時変化率（％）を測定した結果を表５、図４及び図５に示す。図中、「７無添加」とは、組成Ｎｏ．７に何も添加していないことを現し、「７＋ＮｉＯ」とは、組成Ｎｏ．７にＮｉＯを添加したことを現す。尚、図４のデータを表記しなかったが、初期値に対して２０％減少したところで定常状態となっていることが図４から明らかである。

【００１８】

【表４】

NiO量 [wt%]	εr	Kr[%]	Qm	Tc[℃]
0．2	７５０	３９	１９０	２７４
0．5	７８０	４２	１６０	２６９
1．0	７９０	４７	１６０	２６５
3．0	８４０	４７	１６０	２５７
5．0	９９０	４５	１５０	２３８

【表５】

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時間 [hr]	素子	ＮｉＯ添加量［重量％］				
		０．２	０．５	１．０	３．０	５．０
初期	A	200	160	160	170	150
	B	190	160	180	160	150
119	A	-26	-7	-6	-10	-8
	B	-23	-9	-6	-5	-5
453	A	-68	-5	-6	-3	-7
	B	-52	-3	-1	-1	-6
548	A	-74	-6	-9	-3	-7
	B	-56	-4	-3	0	-3
1046	A	-85	-11	-16	-5	-9
	B	-71	-9	-9	-5	-5

表４、表５、図４及び図５にみられるように、基本組成Ｎｏ．７に対してもＮｉＯを所定量添加しただけで、Ｑｍを下げながらεｒとＫｒを向上させ、更に高湿度下でのＱｍの経時変化を抑制することができた。

【００１９】－比較例１－

本例は、実施例１の基本組成Ｎｏ．６またはＮｏ．７にMnO_2を添加したセラミックフィルタ素子用圧電磁器について、その諸特性を評価したものである。すなわち、前記表１及び図１の組成Ｎｏ．６またはＮｏ．７となるように秤量した原料１００％に対して、純度９４％のMnO_2を所定量添加した以外は、実施例１と同様の方法にてセラミックフィルタ素子用圧電磁器を製造した。このセラミックフィルタ素子用圧電磁器について、εｒ、Ｋｒ、Ｑｍ及びキュリー点Ｔｃを測定した結果を表６（基本組成Ｎｏ．６）及び表８（基本組成Ｎｏ．７）に示す。

【００２０】また、基本組成Ｎｏ．６にMnO_2を添加した磁器につき、６０℃、相対湿度９５％の雰囲気中でのＱｍの初期値に対する経時変化率（％）を測定した結果を表７及び図６に示し、基本組成Ｎｏ．７にMnO_2を添加した磁器につき、同様に測定した結果を表９及び図７に示す。図中、「６＋MnO_2」とは、組成Ｎｏ．６にMnO_2を添加したことを現し、「７＋MnO_2」とは、組成Ｎｏ．７にMnO_2を添加したことを現す。

【００２１】

【表６】

MnO_2量 [wt%]	εｒ	Ｋｒ[％]	Ｑｍ	Ｔｃ[℃]
０．２	１８００	６１	７５０	２３７
０．５	１２００	５８	１２００	２３１
１．０	９２０	５２	１３００	２１８
３．０	６７０	４２	６５０	１８１

【表７】

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時間 [hr]	素子	MnO_2添加量［重量%］ 0．2	0．5	1．0	3．0
初期	A	760	1300	1200	690
	B	490	1100	1400	680
117	A	-47	-33	-24	-16
	B	-13	-44	-24	-21
233	A	-61	-35	-34	-9
	B	-30	-41	-44	-17
283	A	-36	0	-18	-10
	B	+7	-11	-17	-28
470	A	-39	-17	-16	-10
	B	-9	+32	-24	-14

【表８】

MnO_2量 [wt%]	εr	Kr[%]	Qm	Tc[℃]
0．2	650	51	410	263
0．5	550	42	720	260
1．0	520	48	2500	242
3．0	510	41	750	207

＊【表９】

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＊

時間 [hr]	素子	MnO_2添加量［重量%］ 0．2	0．5	1．0	3．0
初期	A	180	720	1300	650
	B	420	130	2500	750
122	A	-20	-11	-1	-3
	B	-35	-9	-44	-13
472	A	-6	-2	+5	+9
	B	-19	-7	-46	-6
574	A	-11	+3	+42	+6
	B	-27	-10	-23	-15
1115	A	-12	+3	+170	+11
	B	-18	-15	+53	-14

表６～９及び図６，７にみられるように、基本組成Ｎｏ．６及びＮｏ．７のいずれに対してMnO_2を添加しても、初期Ｑｍがかえって大きくなるばかりか、εｒとＫｒの向上も認められず、更に高湿度下でのＱｍの経時変化を抑制することもできなかった。

【００２２】－比較例２－

本例は、実施例１の基本組成Ｎｏ．６またはＮｏ．７にＣｏＯを添加したセラミックフィルタ素子用圧電磁器に

ついて、その諸特性を評価したものである。すなわち、前記表１及び図１の組成Ｎｏ．６またはＮｏ．７となるように秤量した原料１００％に対して、純度９７．８％のＣｏＯを所定量添加した以外は、実施例１と同様の方法にてセラミックフィルタ素子用圧電磁器を製造した。このセラミックフィルタ素子用圧電磁器について、εr、Ｋr、Ｑm及びキュリー点Ｔcを測定した結果を表１０（基本組成Ｎｏ．６）及び表１２（基本組成Ｎｏ．１３）に示す。

【００２３】また、基本組成Ｎｏ．６にＣｏＯを添加した磁器につき、６０℃、相対湿度９５％の雰囲気中でのＱmの初期値に対する経時変化率（％）を測定した結果を表１１及び図８に示し、基本組成Ｎｏ．７にＣｏＯを添加した磁器につき、同様に測定した結果を表１３及び図９に示す。図中、「６＋ＣｏＯ」とは、組成Ｎｏ．６にＣｏＯを添加したことを現し、「７＋ＣｏＯ」とは、＊組成Ｎｏ．７にＣｏＯを添加したことを現す。

【００２４】

【表１０】

CoO量 [wt%]	εr	Kr[%]	Qm	Tc[℃]
0．2	１９００	６３	４９０	２４３
0．5	２２００	６２	３６０	２３９
1．0	２４００	５８	２００	２３３
3．0	分　極　不　能			２３１

【表１１】

時間 [hr]	素子	ＣｏＯ添加量［重量％］ 0．2	0．5	1．0	3．0
初期	A	530	360	210	測定せず
	B	460	380	210	
70	A	-26	-23	-3	
	B	-37	-35	-12	
131	A	-38	-20	+12	
	B	-23	-13	+10	
378	A	-18	+3	+1	
	B	-19	-1	+1	
953	A	-5	+6	+20	
	B	+17	-1	+18	

【表１２】

CoO量 [wt%]	εr	Kr[%]	Qm	Tc[℃]
0．2	５５０	５１	８００	２７０
0．5	５１０	４８	５３０	２７１
1．0	５１０	４７	６００	２６７
3．0	分　極　不　能			２６３

【表１３】

13　　14

時間 [hr]	素子	CoO添加量［重量%］ 0．2	0．5	1．0	3．0
初期	A	810	560	650	
	B	760	500	580	
134	A	-17	-21	-16	測定せず
	B	-3	+3	-6	
188	A	+10	-5	-10	
	B	+14	+6	+4	
380	A	-41	-16	-13	
	B	-15	-7	-8	
997	A	-84	-27	-13	
	B	-69	-26	-14	

表１０～１３及び図８，９にみられるように、基本組成Ｎｏ．６及びＮｏ．７のいずれに対してＣｏＯを添加しても、初期Ｑｍがかえって大きくなるばかりか、εｒとＫｒの向上も認められず、更に高湿度下でのＱｍの経時変化を抑制することもできなかった。

【００２５】

【発明の効果】以上のように、この発明の圧電磁器組成物は、機械的品質係数が小さく、誘電率と電気機械結合係数が高いので、これをセラミックフィルタ素子に適用すれば、位相歪が小さく、群遅延時間特性に優れたものとなり、しかも耐湿性が著しく改善されているので、長期間その特性を維持することができる。

【図面の簡単な説明】

【図１】この発明の圧電磁器組成物の基本組成物の範囲を示す３成分系組成図である。

【図２】基本組成物Ｎｏ．６のみからなる圧電磁器組成物のＱｍの高湿度下における経時変化を示すグラフである。

【図３】基本組成物Ｎｏ．６にＮｉＯを添加した圧電磁器組成物のＱｍの高湿度下における経時変化を示すグラフである。

【図４】基本組成物Ｎｏ．７のみからなる圧電磁器組成物のＱｍの高湿度下における経時変化を示すグラフである。

【図５】基本組成物Ｎｏ．７にＮｉＯを添加した圧電磁器組成物のＱｍの高湿度下における経時変化を示すグラフである。

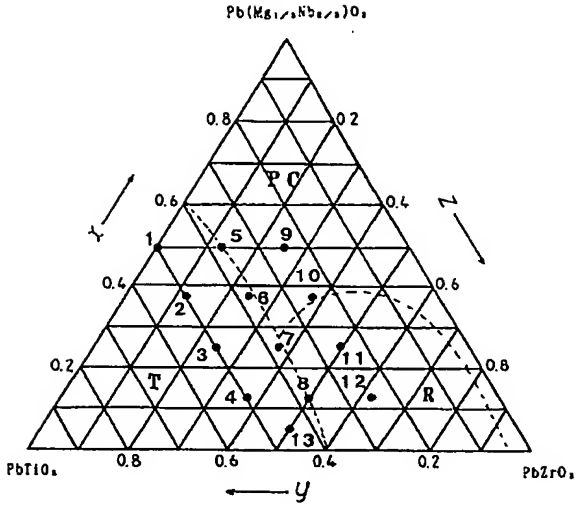
【図６】基本組成物Ｎｏ．６にMnO_2を添加した圧電磁器組成物のＱｍの高湿度下における経時変化を示すグラフである。

【図７】基本組成物Ｎｏ．７にMnO_2を添加した圧電磁器組成物のＱｍの高湿度下における経時変化を示すグラフである。

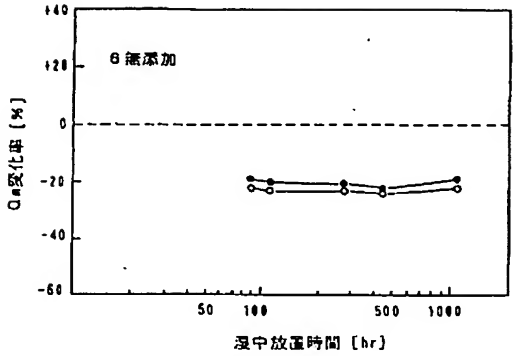
【図８】基本組成物Ｎｏ．６にＣｏＯを添加した圧電磁器組成物のＱｍの高湿度下における経時変化を示すグラフである。

【図９】基本組成物Ｎｏ．７にＣｏＯを添加した圧電磁器組成物のＱｍの高湿度下における経時変化を示すグラフである。

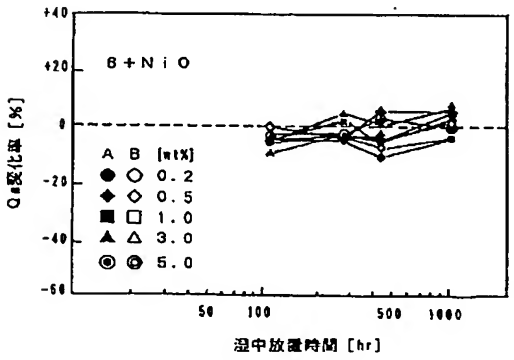
【図1】



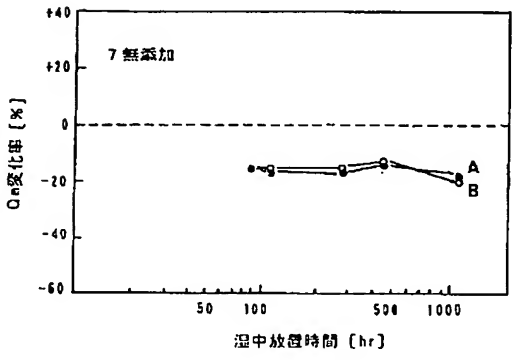
【図2】



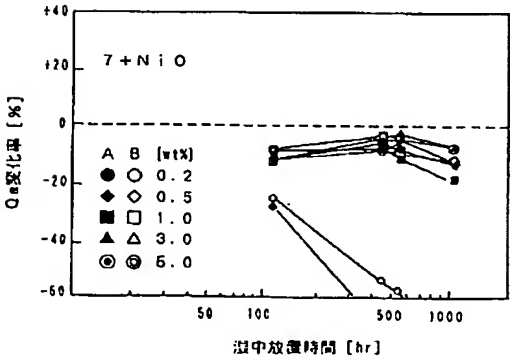
【図3】



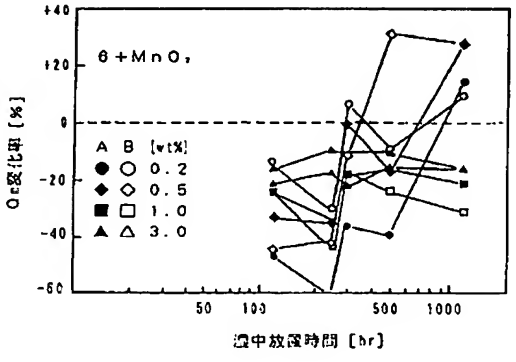
【図4】



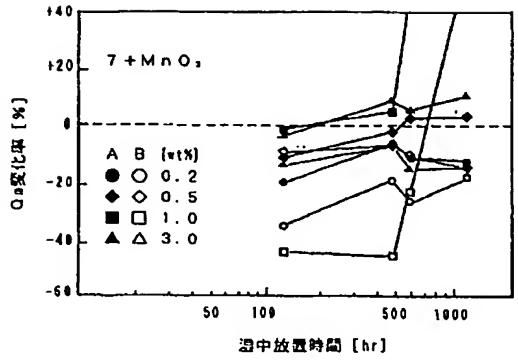
【図5】



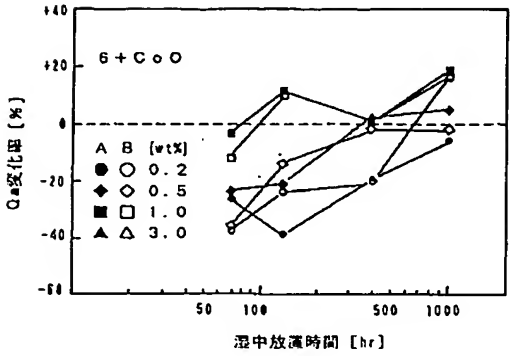
【図6】



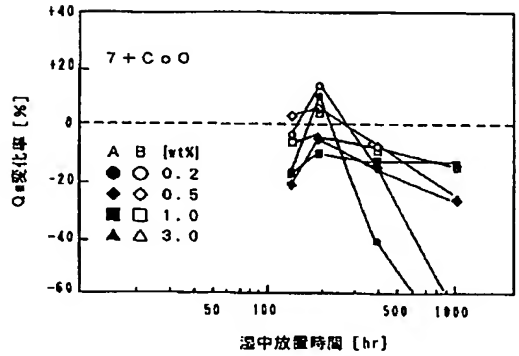
【図７】


7＋MnO₂
A B [wt%]
0.2
0.5
1.0
3.0
Qm変化率 [%]
湿中放置時間 [hr]

【図８】


6＋CoO
A B [wt%]
0.2
0.5
1.0
3.0
Qm変化率 [%]
湿中放置時間 [hr]

【図９】


7＋CoO
A B [wt%]
0.2
0.5
1.0
3.0
Qm変化率 [%]
湿中放置時間 [hr]

JAPANESE [JP,07-315926,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS OPERATION EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] The piezoelectric-ceramics constituent for ceramic filter components excellent in the moisture resistance characterized by carrying out content of the NiO 5 or less (however, 0 being removed) % of the weight to the basic constituent with which a general formula is shown by xPb(Mg1/3Nb 2/3) O3-yPbTiO3-zPbZrO3, and consists of 0.05<=x<=0.50, 0.25<=y<=0.50, and 0<=z<=0.625. However, x, and y and z are numbers which satisfy x+y+z=1 among a general formula.
[Claim 2] The piezoelectric-ceramics constituent for ceramic filter components excellent in the moisture resistance according to claim 1 whose filter is a ladder filter.
[Claim 3] The piezoelectric-ceramics constituent for ceramic filter components which is on the phase transition boundary line inserted by x= 0.375, y= 0.375, the first presentation that consists of z= 0.250, and the second presentation which consists of x= 0.250, y= 0.375, and z= 0.375, and was excellent in the moisture resistance according to claim 2 which makes other constituents near a parallel resonance child and the second presentation a series resonance child for the constituent near the first presentation.

[Translation done.]

JAPANESE [JP,07-315926,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS OPERATION EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the piezoelectric-ceramics constituent for ceramic filter components excellent in moisture resistance. This piezoelectric-ceramics constituent may be used like the super-thin filter for cellular, and the thin filter for pagers suitable for the ladder filter whose intermediate frequency is 455kHz.
[0002]
[Description of the Prior Art] What has high [as much as possible] dielectric constant epsilonr and the direction electromechanical coupling coefficient Kr of a path and still as small [phase distortion is small, and] as this kind of a piezoelectric-ceramics constituent the mechanical quality factor Qm to an anti-humidity load test and its rate of change as possible is desired. Titanic-acid lead zirconate Pb(TixZr 1-x) O3 which has the presentation near the phase transition boundary line (MPB) in order to attain some of these requests (it is hereafter written as PZT.) However, it is x=0.4-0.6. It considers as a basic presentation and the proposal which is going to tune each property finely with various additives is made.

[0003] For example, the piezoelectric-ceramics constituent for ceramic filter components which raised moisture resistance is indicated by JP,5-9072,A by considering as many PZT constituents of Pb5CrO8 among [CrO /5 / Pb2] the resultants of chrome oxide and lead oxide. Moreover, the piezoelectric-ceramics constituent for ceramic filter components made small is indicated [rate / of degradation / of Kr in a large elevated temperature] by JP,5-148016,A in Kr by permuting some Pb atoms of PZT by Ba etc., considering the field by the side of a tetragonal-system ferroelectric phase as a basic presentation, and carrying out minute amount addition of the hard-ized agents, such as software-ized agents, such as Sb, and Co, rather than MPB, at this.
[0004]
[Problem(s) to be Solved by the Invention] However, as for the thing given in JP,5-9072,A, the examination about Kr is not made. Moreover, as for the thing given in JP,5-148016,A, a damp-proof examination is not made. Furthermore, since all are considering PZT as the basic presentation, PZT is not exceeded about a piezo-electric property.
[0005] The purpose of this invention is to offer the piezoelectric-ceramics [with high and Kr] constituent for ceramic filter components with Qm small also under high humidity on the basis of a different presentation from PZT.
[0006]
[Means for Solving the Problem] In order to attain that purpose, it is characterized by the piezoelectric-ceramics constituent for ceramic filter components of this invention carrying out content of the NiO 5 or less (however, 0 being removed) % of the weight to the basic constituent which a general formula is shown by xPb(Mg1/3Nb 2/3) O3-yPbTiO3-zPbZrO3, and consists of 0.05<=x<=0.50, 0.25<=y<=0.50, and 0<=z<=0.625. However, x, and y and z are numbers which satisfy x+y+z=1 among a general formula.
[0007]

[Function] The above-mentioned basic constituent has low Qm, and its Kr is high. And since epsilonr changes on MPB, suitable epsilonr can be chosen by changing a basic presentation according to the applications, such as an object for juxtaposition, and an object for serials, for example in a ladder filter. And if specified quantity addition of the NiO is carried out at this basic constituent, Kr can be raised as epsilonr, lowering Qm and the resistance to humidity of Qm can also be raised further. In addition, the reason which limited x, and y and z to the above-mentioned specific range, respectively is as follows among the general formula of this invention.
[0008] That is, high Tc will not be obtained if a degree of sintering is bad if x does not fulfill 0.05, and 0.50 is exceeded. Moreover, unless y fulfills 0.25, high Tc is not obtained, and if 0.50 is exceeded, epsilonr [high] and high Kr will not be obtained. Although zero of z are also still more satisfactory practically, high Tc will not be obtained if 0.625 is exceeded. Furthermore, since Tc fell as the addition increased, NiO added to these basic presentation was taken as to a maximum of 5 % of the weight.
[0009]
[Example]
- The example of an example 1-book illustrates the addition effectiveness of the manufacture approach of the piezoelectric-ceramics constituent this invention, and NiO while deciding the range of a basic presentation.
[0010] Lead oxide PbO of decision of a basic presentation, and the 99.3% of the [manufacture approach] purity, the magnesium oxide MgO of 99.4% of purity, Niobium oxide Nb 2O5 of 99.5% of purity, titanium oxide TiO2 of 98.5% of purity, and the zirconium dioxide ZrO2 of 99.0% of purity are prepared, respectively at a preparation rate corresponding to the presentation of presentation No.1-13 shown in Table 1 and drawing 1 . After carrying out dry-blending grinding in the vibration mill with the alumina ball and carrying out temporary quenching of the mixture at 850 degrees C for 2 hours, the slurry was obtained by carrying out wet blending by 90rpm with ion exchange water besides an alumina ball, an organic binder, etc. with a pot rotating machine for 23 hours. In addition, a strong dielectric tetragonal phase (ferroelectric tetragonal) and R of T are the elision marks of strong dielectric rhombohedral (ferroelectric rhombohedral) one and a pseudo-cubic [PC / dielectricity / strong] (ferroelectric pseudocubic) among drawing 1 .
[0011] After freeze-drying the slurry at -40 degrees C among the vacuum of 0.4 or less Torrs and passing the sieve of 500 micrometers of apertures, it fabricated by the pressure of 1 t/cm2 to disc-like [with a diameter / of 25mm / x thickness of 2mm], and calcinated at 1300 degrees C for 2 hours. Then, after grinding a baking object until it became 1mm in thickness, the electrode pattern with a diameter of 18mm was screen-stenciled to both the principal plane with Ag paste, and it was able to be burned at 720 degrees C. And this was immersed into the 100 degrees C - 150 degrees C silicone oil, and it polarized by impressing the direct current voltage of 30 kV/cm to inter-electrode for 30 minutes, and considered as the piezoelectric ceramics for ceramic filter components. The above production process is the same except for an additive being added in a preparation phase also in each below-mentioned example. The result of having measured epsilonr, and Qm, Kr and Tc about the obtained piezoelectric ceramics is shown in Table 1.
[0012]
[Table 1]

組成 No.	組成 [mol分率] PMN	PT	PZ	Qm	Kr [%]	εr	Tc [℃]
1	.500	.500	0	320	22	890	253
2	.375	.500	.125	330	15	700	283
3	.250	.500	.250	330	16	800	316
4	.125	.500	.375	320	17	900	351
5	.500	.375	.125	100	46	3200	219
6	.375	.375	.250	170	56	2000	245
7	.250	.375	.375	150	30	770	278
8	.125	.375	.500	180	24	700	313
9	.500	.250	.250	190	42	840	226
10	.375	.250	.375	200	40	640	206
11	.250	.250	.500	220	34	500	263
12	.125	.250	.625	250	19	530	293
13	.050	.450	.500	170	48	1200	366

[注] 表中、PMN、PT及びPZは、それぞれ$Pb(Mg_{1/3}Nb_{2/3})O_3$、$PbTiO_3$及び$PbZrO_3$を表す。

it sees in Table 1 -- as -- the basic presentation range of this invention -- especially -- presentation No. near [the] MPB -- in 5 and 6, Qm is small, Kr is high and epsilonr is also high. Moreover, it also turned out that epsilonr has changed suddenly between presentation No.6 and presentation No.7. Therefore, if the side near the object for parallel resonance children and No.7 is chosen for the side near No.6 among the presentations on the line which connects these two points as an object for series resonance children, it is small as much as possible in Qm, and it is clear [maintaining Kr as highly as possible] that the porcelain possessing desired epsilonr is obtained.

[0013] The piezoelectric ceramics for ceramic filter components were manufactured by the same approach as the above to 100% of raw materials which carried out weighing capacity so that it might be set to presentation No.6 of the [example of addition of NiO] above except having carried out specified quantity addition of the NiO of 97% of purity. About these piezoelectric ceramics for ceramic filter components, the result of having measured epsilonr, Kr and Qm, and Curie point Tc is shown in Table 2.

[0014] Moreover, the result of having measured the rate of aging to the initial value of Qm in the inside of 60 degrees C and the ambient atmosphere of 95% of relative humidity (%) is shown in Table 3, drawing 2 , and drawing 3 . Among drawing, it means that nothing has added to presentation No.6, and expresses having added NiO to presentation No.6 as "6 Additive-free" with "6+NiO." In addition, although the data of drawing 2 were not written, it is clear from drawing 2 that it is a steady state in the place which decreased in number 20% to initial value.

[0015]

[Table 2]

NiO量 [wt%]	εr	Kr[%]	Qm	Tc[℃]
0.2	2300	57	120	242
0.5	2600	59	100	237
1.0	2900	61	95	230
3.0	3100	56	100	221
5.0	3200	55	100	205

[Table 3]

時間 [hr]	素子	NiO添加量 [重量%] 0.2	0.5	1.0	3.0	5.0
初期	A	125	107	95	101	102
	B	117	107	97	95	99
114	A	-5	-4	-5	-9	-8
	B	-5	0	-5	-5	-5
280	A	-7	-4	+2	-8	-8
	B	-8	-4	+2	+5	-8
446	A	-10	+6	-2	-4	+2
	B	-7	-5	-7	+1	-4
1043	A	-4	+6	+8	+8	0
	B	-8	+5	+2	+8	+1

Only by carrying out specified quantity addition of the NiO basic presentation No.6, Kr was able to be raised as epsilonr, lowering Qm and aging of Qm under high humidity was able to be further controlled so that Table 2, Table 3, drawing 2 , and drawing 3 might see.

[0016] - The example of an example 2-book evaluates many of the properties about the piezoelectric ceramics for ceramic filter components which added NiO to basic presentation No.7 of an example 1. That is, the piezoelectric ceramics for ceramic filter components were manufactured by the same approach as an example 1 to 100% of raw materials which carried out weighing capacity so that it might be set to presentation No.7 of said table 1 and drawing 1 except having carried out specified quantity addition of the NiO of 97% of purity. About these piezoelectric ceramics for ceramic filter components, the result of having measured epsilonr, Kr and Qm, and Curie point Tc is shown in Table 4.

[0017] Moreover, the result of having measured the rate of aging to the initial value of Qm in the inside of 60 degrees C and the ambient atmosphere of 95% of relative humidity (%) is shown in Table 5, drawing 4 , and drawing 5 . Among drawing, it means that nothing has added to presentation No.7, and expresses having added NiO to presentation No.7 as "7 Additive-free" with "7+NiO." In addition, although the data of drawing 4 were not written, it is clear from drawing 4 that it is a steady state in the place which decreased in number 20% to initial value.

[0018]

[Table 4]

NiO量 [wt%]	εr	Kr[%]	Qm	Tc[℃]
0.2	750	39	190	274
0.5	780	42	160	269
1.0	790	47	160	265
3.0	840	47	160	257
5.0	990	45	150	238

[Table 5]

時間 [hr]	素子	NiO添加量 [重量%] 0.2	0.5	1.0	3.0	5.0
初期	A	200	160	160	170	150
	B	190	160	160	160	150
119	A	-26	-7	-6	-10	-8
	B	-23	-9	-6	-5	-5
453	A	-68	-5	-6	-3	-7
	B	-52	-3	-1	-1	-8
548	A	-74	-6	-9	-9	-7
	B	-56	-4	-8	0	-8
1046	A	-85	-11	-16	-5	-9
	B	-71	-9	-9	-5	-5

Only by carrying out specified quantity addition of the NiO also to basic presentation No.7, Kr was able to be raised as epsilonr, lowering Qm and aging of Qm under high humidity was able to be further controlled so that Table 4, Table 5, drawing 4 , and drawing 5 might see.

[0019] - The example of an example of comparison 1-book evaluates many of the properties about the piezoelectric ceramics for ceramic filter components which added MnO2 to basic presentation No.6 of an example 1, or No.7. That is, the piezoelectric ceramics for ceramic filter components were manufactured by the same approach as an example 1 to 100% of raw materials which carried out weighing capacity so that it might be set to presentation No.6 of said table 1 and drawing 1 , or No.7 except having carried out specified quantity addition of MnO2 of 94% of purity. About these piezoelectric ceramics for ceramic filter components, the result of having measured epsilonr, Kr and Qm, and Curie point Tc is shown in Table 6 (basic presentation No.6) and 8 (basic presentation No.7).

[0020] Moreover, the result of having measured the rate of aging to the initial value of Qm in the inside of 60 degrees C and the ambient atmosphere of 95% of relative humidity (%) is shown in Table 7 and drawing 6 about the porcelain which added MnO2 to basic presentation No.6, and the result measured similarly is shown in Table 9 and drawing 7 about the porcelain which added MnO2 to basic presentation No.7. Among drawing, it means having added MnO2 to presentation No.6, and expresses

having added MnO2 to presentation No.7 as "6+MnO2" with "7+MnO2."

[0021]

[Table 6]

MnO2量 [wt%]	εr	Kr[%]	Qm	Tc[℃]
0.2	1800	61	750	237
0.5	1200	58	1200	231
1.0	920	52	1300	218
3.0	670	42	650	181

[Table 7]

時間 [hr]	素子	MnO2添加量 [重量%] 0.2	0.5	1.0	3.0
初期	A	760	1300	1200	630
	B	490	1100	1400	680
117	A	-47	-33	-24	-16
	B	-13	-44	-24	-21
233	A	-61	-35	-34	-9
	B	-30	-41	-44	-17
283	A	-36	0	-18	-10
	B	+7	-11	-17	-22
470	A	-39	-17	-15	-10
	B	-9	+32	-24	-14

[Table 8]

MnO2量 [wt%]	εr	Kr[%]	Qm	Tc[℃]
0.2	650	51	410	263
0.5	550	42	720	260
1.0	520	48	2500	242
3.0	510	41	750	207

[Table 9]

時間 [hr]	素子	MnO2添加量 [重量%] 0.2	0.5	1.0	3.0
初期	A	180	720	1300	650
	B	420	130	2500	750
122	A	-20	-11	-1	-3
	B	-35	-9	-44	-13
472	A	-6	-2	+5	+9
	B	-19	-7	-46	-6
574	A	-11	+3	+42	+6
	B	-27	-10	-23	-15
1115	A	-12	+3	+170	+11
	B	-18	-15	+53	-14

As seen in Tables 6-9 and drawing 6 , and 7, even if it added MnO2 to any of basic presentation No.6 and No.7, improvement in Kr was not accepted to be about [becoming rather large] and epsilonr, either, and Qm was not able to control aging of Qm under high humidity further the first stage, either.
[0022] - The example of an example of comparison 2-book evaluates many of the properties about the piezoelectric ceramics for ceramic filter components which added CoO to basic presentation No.6 of an example 1, or No.7. That is, the piezoelectric ceramics for ceramic filter components were manufactured by the same approach as an example 1 to 100% of raw materials which carried out weighing capacity so that it might be set to presentation No.6 of said table 1 and drawing 1 , or No.7 except having carried out specified quantity addition of the CoO of 97.8% of purity. About these piezoelectric ceramics for ceramic filter components, the result of having measured epsilonr, Kr and Qm, and Curie point Tc is shown in Table 10 (basic presentation No.6) and 12 (basic presentation No.13).
[0023] Moreover, the result of having measured the rate of aging to the initial value of Qm in the inside of 60 degrees C and the ambient atmosphere of 95% of relative humidity (%) is shown in Table 11 and drawing 8 about the porcelain which added CoO to basic presentation No.6, and the result measured similarly is shown in Table 13 and drawing 9 about the porcelain which added CoO to basic presentation No.7. Among drawing, it means having added CoO to presentation No.6, and expresses having added CoO to presentation No.7 as "6+CoO" with "7+CoO."
[0024]
[Table 10]

CoO量 [wt%]	εr	Kr[%]	Qm	Tc[℃]
0.2	1900	63	490	243
0.5	2200	62	360	239
1.0	2400	58	200	238
3.0	分極不能			231

[Table 11]

時間 [hr]	素子	CoO添加量［重量%］ 0．2	0．5	1．0	3．0
初期	A	530	360	210	測定せず
	B	460	360	210	
70	A	-26	-23	-3	
	B	-37	-35	-12	
191	A	-38	-20	+12	
	B	-29	-13	+10	
378	A	-18	+3	+1	
	B	-19	-1	+1	
953	A	-5	+6	+20	
	B	+17	-1	+18	

[Table 12]

CoO量 [wt%]	σr	Kr[%]	Qm	Tc[℃]
0．2	550	51	800	270
0．5	510	48	530	271
1．0	510	47	600	267
3．0	分極不能			263

[Table 13]

時間 [hr]	素子	CoO添加量［重量%］ 0．2	0．5	1．0	3．0
初期	A	810	560	650	測定せず
	B	760	500	580	
134	A	-17	-21	-16	
	B	-3	+3	-6	
188	A	+10	-5	-10	
	B	+14	+6	+4	
380	A	-41	-16	-13	
	B	-15	-7	-8	
997	A	-84	-27	-13	
	B	-69	-26	-14	

As seen in Tables 10-13 and drawing 8 , and 9, even if it added CoO to any of basic presentation No.6 and No.7, improvement in Kr was not accepted to be about [becoming rather large] and epsilonr, either, and Qm was not able to control aging of Qm under high humidity further the first stage, either.
[0025]
[Effect of the Invention] As mentioned above, since the piezoelectric-ceramics constituent of this invention has a small mechanical quality factor, phase distortion is small if this is applied to a ceramic filter component, since a dielectric constant and the electromechanical coupling coefficient are high, and it becomes the thing excellent in the group delay property and moisture resistance is moreover improved remarkably, that property is maintainable for a long period of time.

[Translation done.]

JAPANESE [JP,07-315926,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS OPERATION EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is 3 component system composition diagram showing the range of the basic constituent of the piezoelectric-ceramics constituent of this invention.
[Drawing 2] It is the graph which shows aging under the high humidity of Qm of the piezoelectric-ceramics constituent which consists only of basic constituent No.6.
[Drawing 3] It is the graph which shows aging under the high humidity of Qm of the piezoelectric-ceramics constituent which added NiO to basic constituent No.6.
[Drawing 4] It is the graph which shows aging under the high humidity of Qm of the piezoelectric-ceramics constituent which consists only of basic constituent No.7.
[Drawing 5] It is the graph which shows aging under the high humidity of Qm of the piezoelectric-ceramics constituent which added NiO to basic constituent No.7.
[Drawing 6] It is the graph which shows aging under the high humidity of Qm of the piezoelectric-ceramics constituent which added MnO2 to basic constituent No.6.
[Drawing 7] It is the graph which shows aging under the high humidity of Qm of the piezoelectric-ceramics constituent which added MnO2 to basic constituent No.7.
[Drawing 8] It is the graph which shows aging under the high humidity of Qm of the piezoelectric-ceramics constituent which added CoO to basic constituent No.6.
[Drawing 9] It is the graph which shows aging under the high humidity of Qm of the piezoelectric-ceramics constituent which added CoO to basic constituent No.7.

[Translation done.]